

# #503: Beyond Li-Ion Batteries for Grid-Scale Energy Storage

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2021 DOE OE Energy Storage Peer-Review  
Virtual, Wednesday, October 27, 2021, 04:25 – 04:40 PM Eastern Time



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# Grid-scale battery energy storage

- Grid-scale energy storage systems converts energy collected from the grid or a power plant into a storable form for later use
- Storage systems are key for grid stability and integration of variable renewable energy sources
- Conventional energy storage technologies are limited by geographical constraints (hydroelectric, compressed air), operational safety concerns and high self-discharge rates (flywheels), and potential lag time between demand and energy supply
- Grid-scale electrochemical energy storage systems (GSEESSs) are not geographically constrained, can be designed safely and with extremely low self discharge rates, and have immediate response times for demand
- GSEESSs stabilize the grid through peak shaving and load leveling, voltage and frequency regulation, and emergency power supply
- **Li-ion represents a significant portion of installed GSEESSs, however due to lifetime, safety, and raw material sourcing concerns, alternative technologies are highly desirable**

# Outline

- Beyond lithium ion cathode investigations
- Mechanistic study of future beyond-lithium ion systems
- Review of current status – Grid Scale Electrochemical Energy Storage Systems

# Strategy

- Leverage knowledge from lithium based electrochemical investigations
- Investigate beyond-lithium ion electrode materials
- Characterize mechanistic function to gain insight regarding functional electrochemistry for beyond-lithium ion batteries
- Consider factors relevant to Grid Scale Electrochemical Energy Storage systems

# Potential Advantages of Mg Based Batteries

Relative to Li based batteries, Mg based batteries have the potential to be less expensive, and have higher volumetric capacity

Property	Mg	Li	Zn
Ionic Radius (pm)	86	90	88
Voltage vs. S.H.E.	-2.37	-3.04	-0.76
Elemental Abundance (ppm in earth's crust)	2.8 x 10 <sup>4</sup>	20	78
Volumetric Capacity (mAh/cm <sup>3</sup> )	3833	2046	5854
Gravimetric Capacity (mAh/g)	2205	3862	820
Volumetric energy (mWh/cm <sup>3</sup> )	9084	6138	4449
Gravimetric energy (mWh/g)	5226	11586	623
\$/lb	\$1.12	\$28	\$1.16

M.H. Huie, D.C. Bock, E.S. Takeuchi, A.C. Marschilok, K.J. Takeuchi\*, *Coordination Chemistry Reviews*, **2015**, 287, 15-27.

# Development of Cathode Materials for Mg batteries

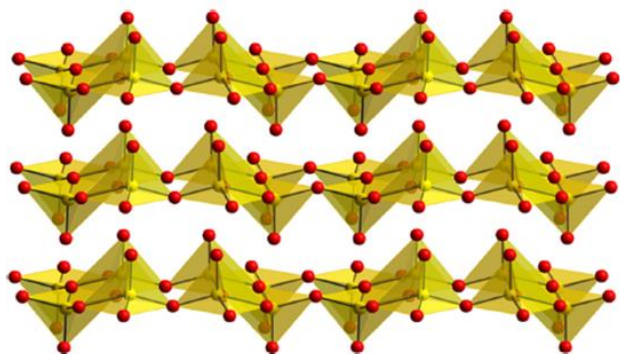
## Key Challenge:

High  $\text{Mg}^{2+}$  valence results in slow solid state diffusion through inorganic cathode materials → low reversible capacity, low power

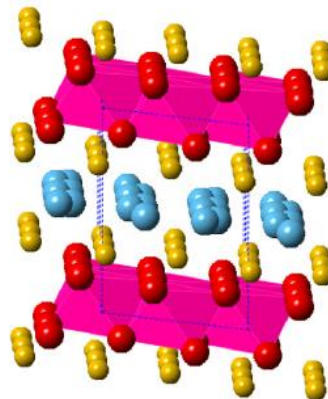
Class	Types of Composition	Formula
Vanadium oxide	Vanadium pentoxide, Magnesiated vanadium pentoxide	$\text{V}_2\text{O}_5$ , $\text{Mg}_x\text{V}_2\text{O}_5$
Manganese oxide	Birnessite, Spinel	$\text{MnO}_2$
Prussian blue	Nickel hexacyanoferrate, Copper hexacyanoferrate	$\text{NiFe}(\text{CN})_6$ , $\text{CuFe}(\text{CN})_6$
Molybdenum sulfide	Chevrel Phase, Molybdenum disulfide	$\text{Mo}_6\text{S}_8$ , $\text{Mo}_6\text{T}_8$ (T = S or Se)
Molybdenum oxide	Orthorhombic	$\text{MoO}_3$

M.H. Huie, D.C. Bock, E.S. Takeuchi, A.C. Marschilok, K.J. Takeuchi\*, *Coordination Chemistry Reviews*, **2015**, 287, 15-27.

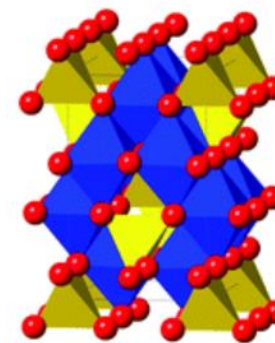
# Cathode Materials for Beyond Li-Ion Electrochemistry



$\text{Mg}_x\text{V}_2\text{O}_5$   
layered  
structure



$\text{Cu}_x\text{MnO}_2$   
 $\text{Mg}_x\text{MnO}_2$   
layered  
structures



$\text{MgMn}_2\text{O}_4$   
spinel  
structure

Y.R. Li, A.S. Poyraz, X. Hu, M. Cuiffo, C. R. Clayton, L. Wu, Y. Zhu, E.S. Takeuchi\*, A.C. Marschilok\*, K.J. Takeuchi\*, *J. Electrochem. Soc.*, **2017**, 164, A2151.

J. Yin, A.B. Brady, E.S. Takeuchi\*, A.C. Marschilok\*, K.J. Takeuchi\*, *Chem. Comm.* **2017**, 53(26), 3665-3668.

J. Yin, E.S. Takeuchi\*, K.J. Takeuchi\*, A.C. Marschilok\*, *Inorg. Chim. Acta*, **2016**, 453, 230-237.

J. Yin, C.J. Pelliccione, S.H. Lee, E.S. Takeuchi\*, K.J. Takeuchi\*, A.C. Marschilok\*, *J. Electrochem. Soc.*, **2016**, 163(9), A1.

# Potential Advantages of Zn Based Batteries

Relative to Li based batteries, Zn based batteries have the potential to be safer, less expensive, and have higher volumetric capacity

Property	Mg	Li	Zn
Ionic Radius (pm)	86	90	88
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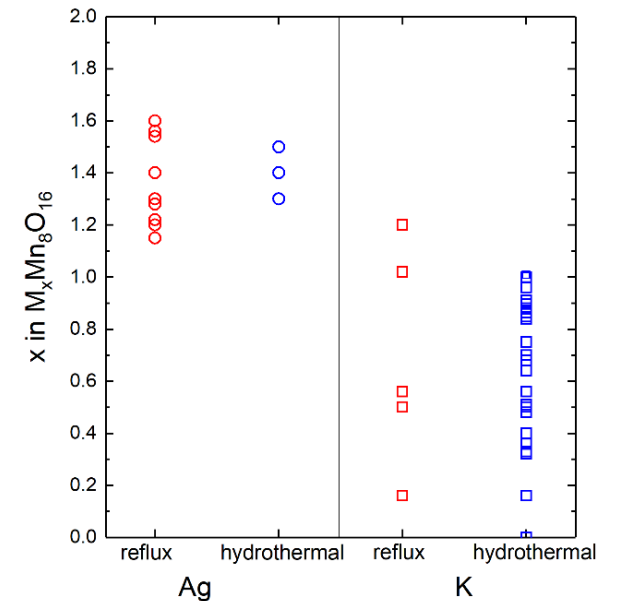
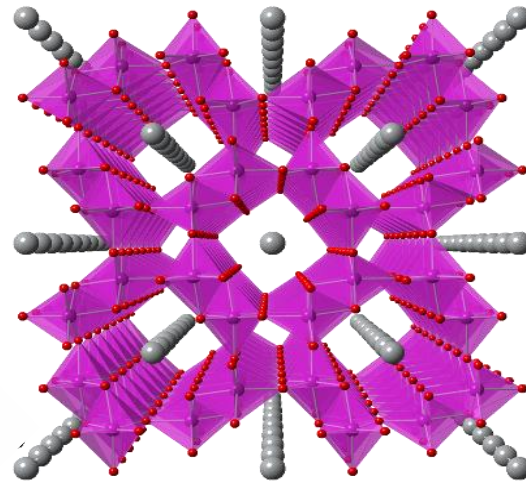
# Aqueous Zinc Battery Cathode: Silver Hollandite ( $\text{Ag}_2\text{Mn}_8\text{O}_{16}$ )

## Motivation:

Aqueous Zn/ $\text{MnO}_2$  batteries are desirable due to high abundance and safety of Zn and  $\text{MnO}_2$

$\alpha$ - $\text{MnO}_2$  is ideal for transport studies as a synthetically tunable model 1D material

In lithium based nonaqueous batteries silver hollandite formed conductive  $\text{Ag}^0$  upon discharge via irreversible reduction-displacement



K.J. Takeuchi\*, S.Z. Yau, M.C. Menard, A.C. Marschilok\*, E.S. Takeuchi\*, *ACS Appl. Mater. Interfaces*, **2012**, 4(10), 5547.

J.L. Durham, A.S. Poyraz, E.S. Takeuchi\*, A.C. Marschilok\*, K.J. Takeuchi\*, *Accounts Chem. Res.*, **2016**, 49(9), 1864.

J.L. Durham, J.P. Huang, B. Zhang, L. Wu, X. Tong, C.J. Pelliccione, Y. Zhu, E.S. Takeuchi\*, A.C. Marschilok\*, K.J. Takeuchi\*, *J. Electrochem. Soc.*, **2017**, 164(14), A3814.

B. Zhang, P.F. Smith, S.-Y. Lee, L. Wu, Y. Zhu, E.S. Takeuchi\*, A.C. Marschilok\*, K.J. Takeuchi, *J. Electrochem. Soc.*, **2017**, 164(1), A6163.

A.B. Brady, J.P. Huang, J.L. Durham, P.F. Smith, J. Bai, E.S. Takeuchi, A.C. Marschilok, K.J. Takeuchi\*, *MRS Advances*, **2018**, 3(10), 547.

J. Huang, L.M. Housel, C.D. Quilty, A.B. Brady, P.F. Smith, A. Abraham, M.R. Dunkin, D.M. Lutz, B. Zhang, E.S. Takeuchi\*, A.C. Marschilok\*, K.J. Takeuchi\*, *J. Electrochem. Soc.*, **2018**, 165(11), A2849-A2858.

P.F. Smith, A.B. Brady, S.-Y. Lee, A.M. Bruck, E. Dooryhee, L. Wu, Y. Zhu, K.J. Takeuchi\*, E.S. Takeuchi\*, A.C. Marschilok\*, *ACS Appl. Mater. Interfac.*, **2018**, 10(1), 400.

L.M. Housel, L. Wang, A. Abraham, J. Huang, G.D. Renderos, C.D. Quilty, A.B. Brady, A.C. Marschilok\*, K.J. Takeuchi\*, E.S. Takeuchi\*, *Accounts Chem. Res.*, **2018**, 51(3), 575.



# Mechanistic characterization of $\text{Ag}_{1.5}\text{Mn}_8\text{O}_{16}$ zincation



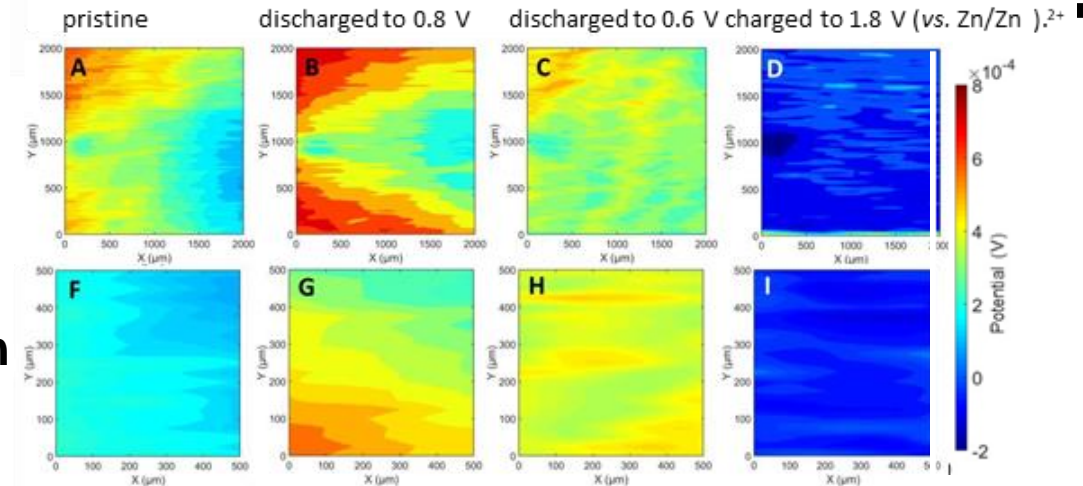
Discharge: charge transfer resistance increased slightly, then decreased significantly.

Charge: impedance increased to approach pristine state

SVP showed increasing DC voltage (increasing current density) upon discharge, with decrease upon charge

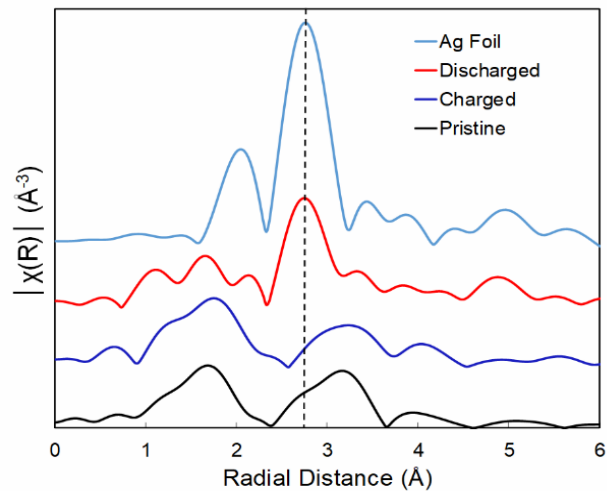
SEM and XAS also consistent with **reversible formation of  $\text{Ag}^0$  on discharge and  $\text{Ag}^+$  on charge**

## Scanning Vibrating Probe (SVP)

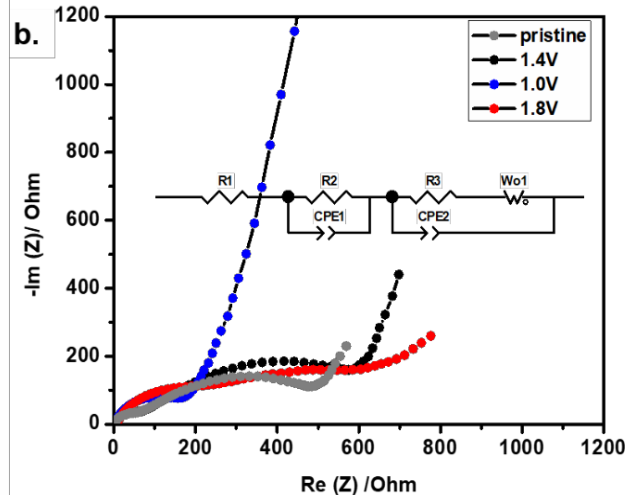


A-D: 2000 x 2000  $\mu\text{m}$  area, F-I: 500 x 500  $\mu\text{m}$  area.

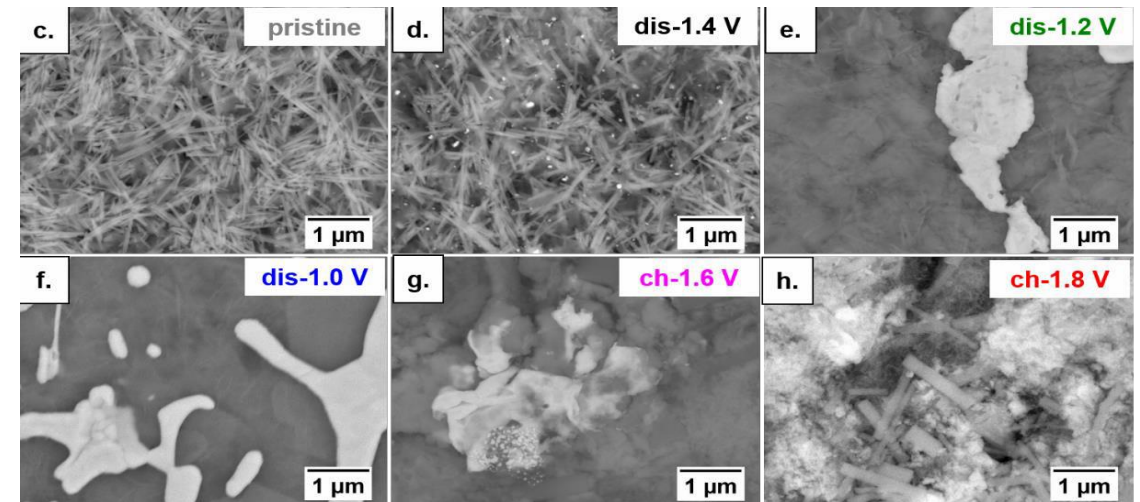
## EXAFS (Ag edge)



## AC Impedance

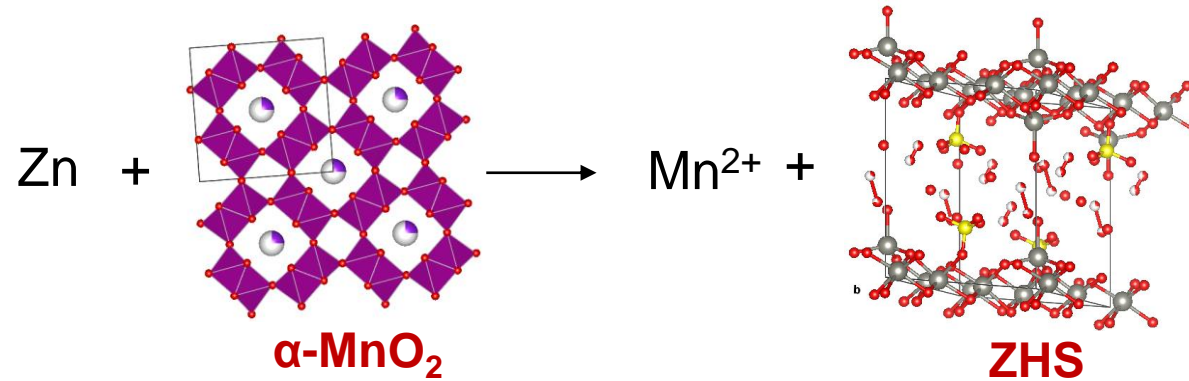


## SEM

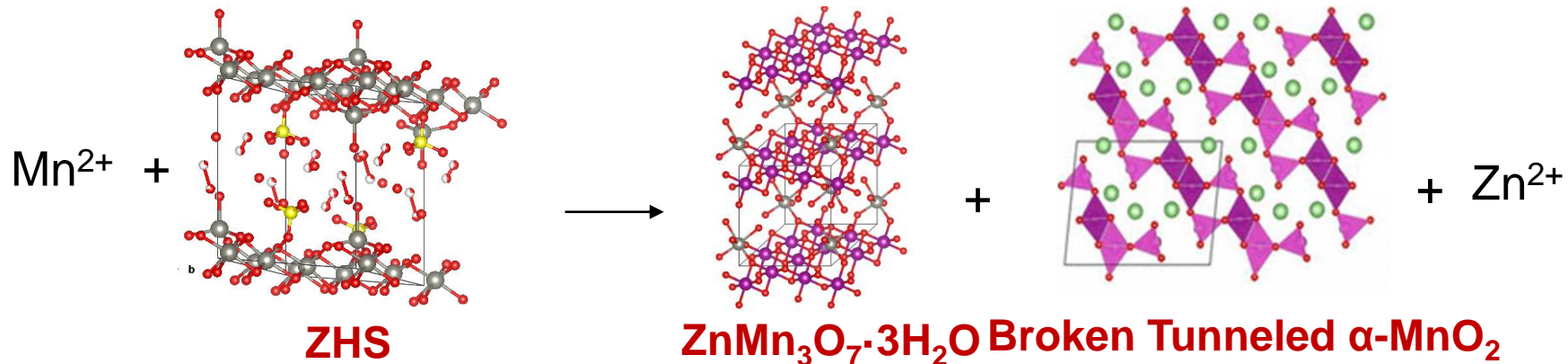


# The Dissolution-Deposition Zn/ $\alpha$ -MnO<sub>2</sub> Mechanism

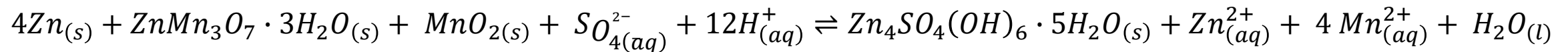
**Discharge** Mn<sup>2+</sup> is dissolved into electrolyte,  $Zn_4SO_4(OH)_6 \cdot 5H_2O_{(s)}$  (ZHS) precipitates on the surface



**Charge** Mn<sup>2+</sup> redeposits as layered  $ZnMn_3O_7 \cdot 3H_2O_{(s)}$  (Chalcophanite) or (broken) tunneled MnO<sub>2</sub> and ZHS dissolves.



## Total Reaction



D. Wu, L.M. Housel, S.-J. Kim, N. Sadique, C.D. Quilty, L. Wu, R. Tappero, S.L. Nicholas, S. Ehrlich, Y. Zhu, A.C. Marschilok, E.S. Takeuchi\*, D.C. Bock\*, K.J. Takeuchi\*, *Energy & Environmental Science*, **2020**, 13, 4322-4333. DOI:10.1039/D0EE02168G

# Grid Scale Electrochemical Energy Storage

## Beyond Li-Ion Batteries for Grid-Scale Energy Storage

### Authors and Affiliations:

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*Lei Wang - Brookhaven National Laboratory*

*Amy C. Marschilok - Brookhaven National Laboratory, Stony Brook University*

### Abstract:

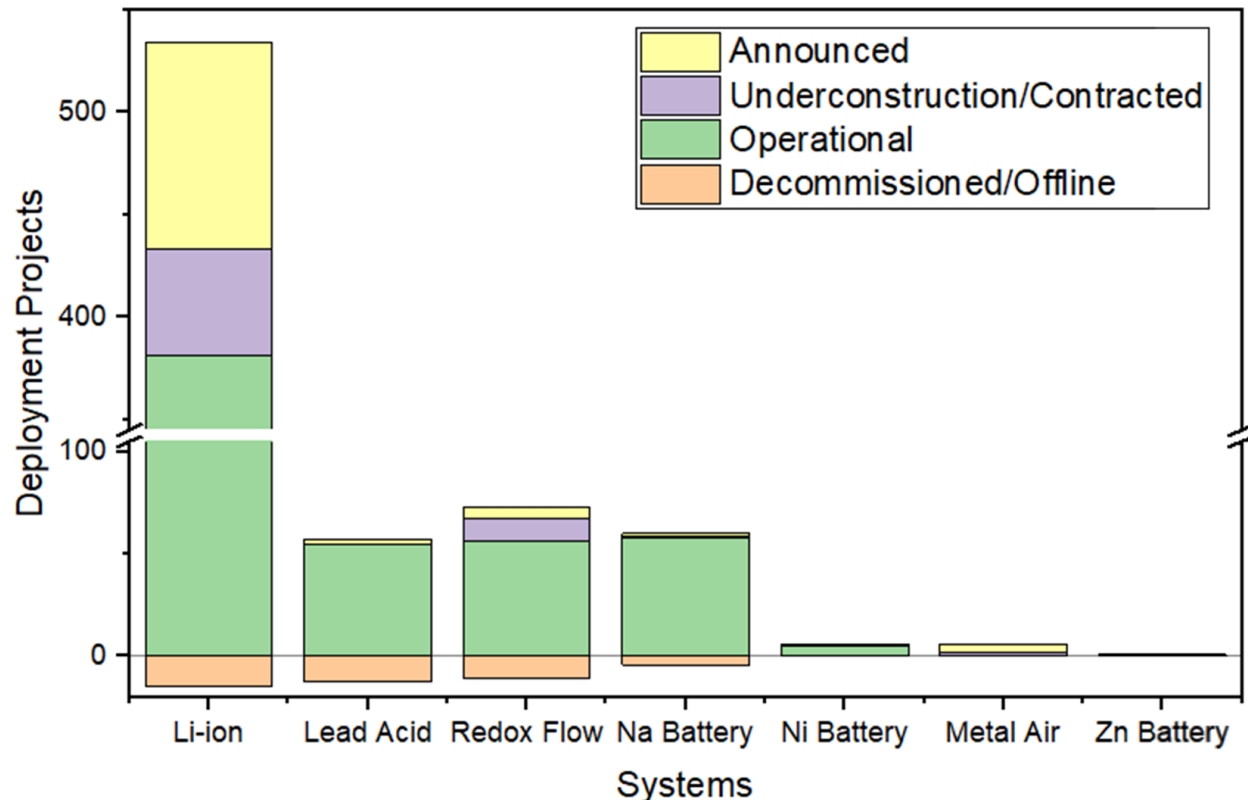
In order to improve resiliency of the grid and enable integration of renewable energy sources into the grid, the utilization of battery systems to store energy for later demand is of the utmost importance. The implementation of grid-scale electrical energy storage systems can aid in peak shaving and load leveling, voltage and frequency regulation, as well as emergency power supply. Although the predominant battery chemistry currently used is Li-ion; due to cost, safety and sourcing concerns, incorporation of other battery technologies is of interest for expanding the breadth and depth of battery storage system installations. Here we discuss existing technologies beyond Li-ion battery storage chemistries that have seen grid-scale deployment, as well as several other promising battery technologies, and analyze their chemistry mechanisms, battery construction and design, and corresponding advantages and disadvantages.

### Contents

1. Introduction
2. Existing battery technologies for grid-scale electrical energy storage
  - 2.1. Aqueous lead acid batteries and Ni based batteries
  - 2.2. Redox flow batteries
  - 2.3. High temperature sodium batteries
3. Potential battery technologies for grid-scale electrical energy storage
  - 3.1. Na-ion batteries
  - 3.2. Rechargeable magnesium batteries
  - 3.3. Rechargeable aqueous zinc batteries
  - 3.4 Metal-air batteries
4. Conclusions
5. Reference

# GSEESS deployment

- Due to lifetime, safety, and raw material sourcing concerns, alternative technologies are desired
- Older technologies (lead acid, high temperature NaS) make up the largest non-Li-ion systems, but many of these older systems are being decommissioned
- Redox flow systems due to their scalability have seen a large increase in interest in recent years and now make up ~10% of the operational systems



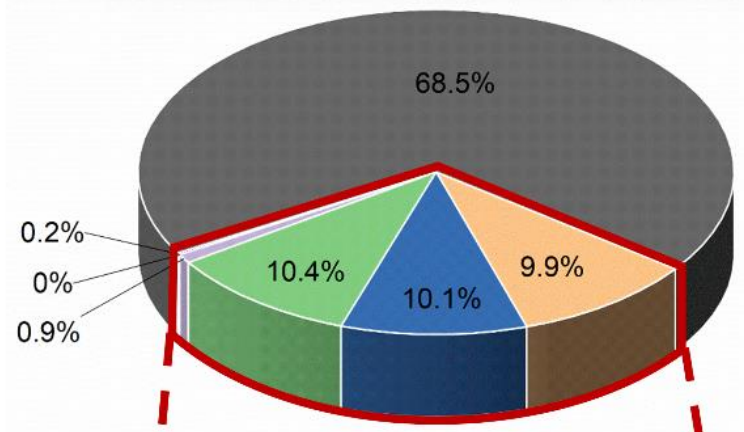
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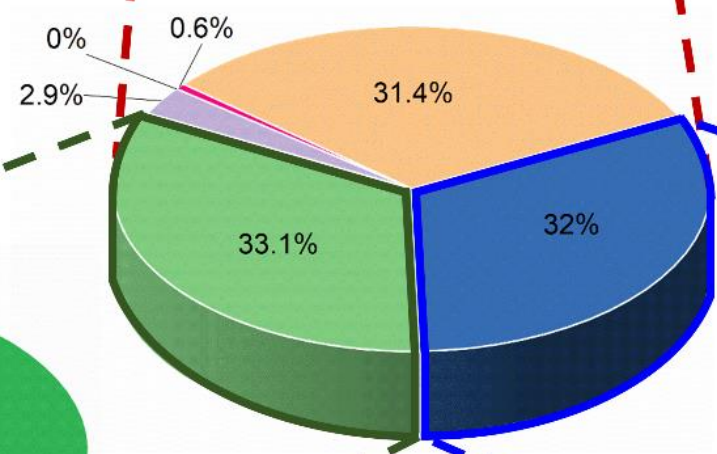
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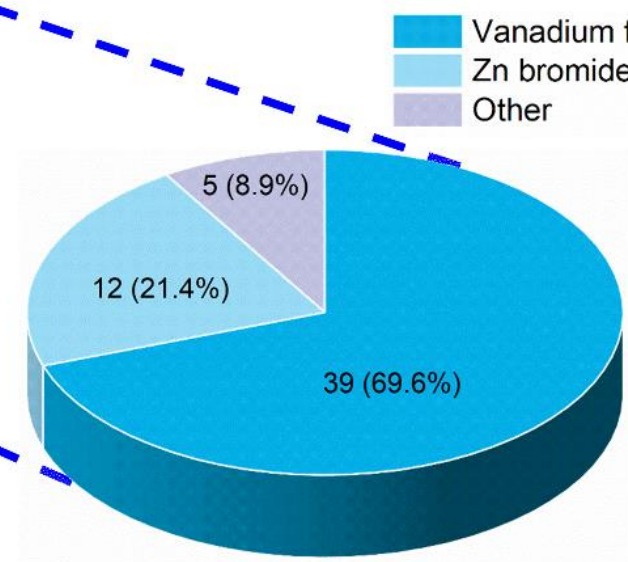
# Operational Energy Storage Systems



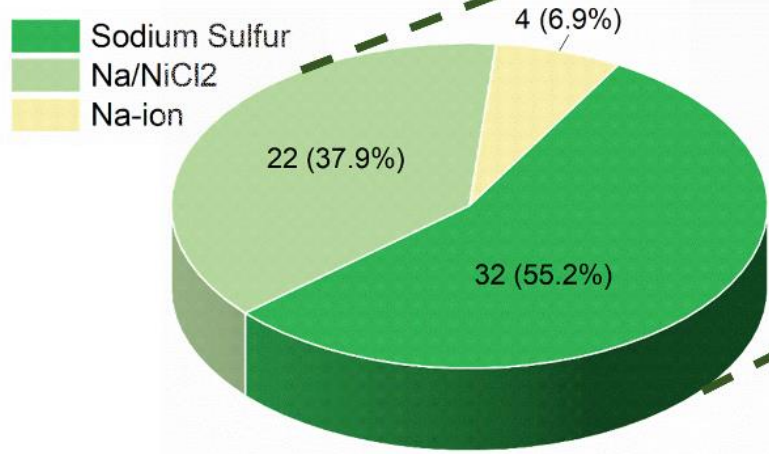
- Li-ion
- Lead Acid
- Redox Flow
- Na Battery
- Ni Battery
- Metal Air
- Zn Battery



- Vanadium flow
- Zn bromide flow
- Other



## Operational BLI Battery Systems

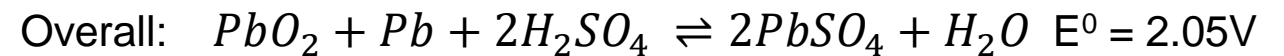
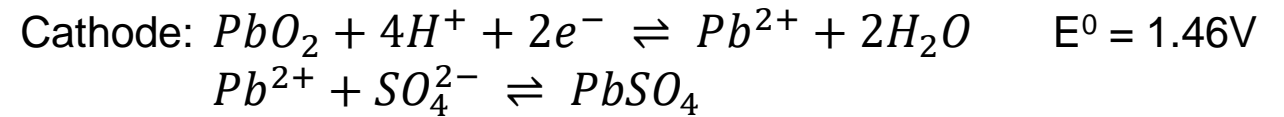


## Sodium Battery Systems

## Redox Flow Battery Systems

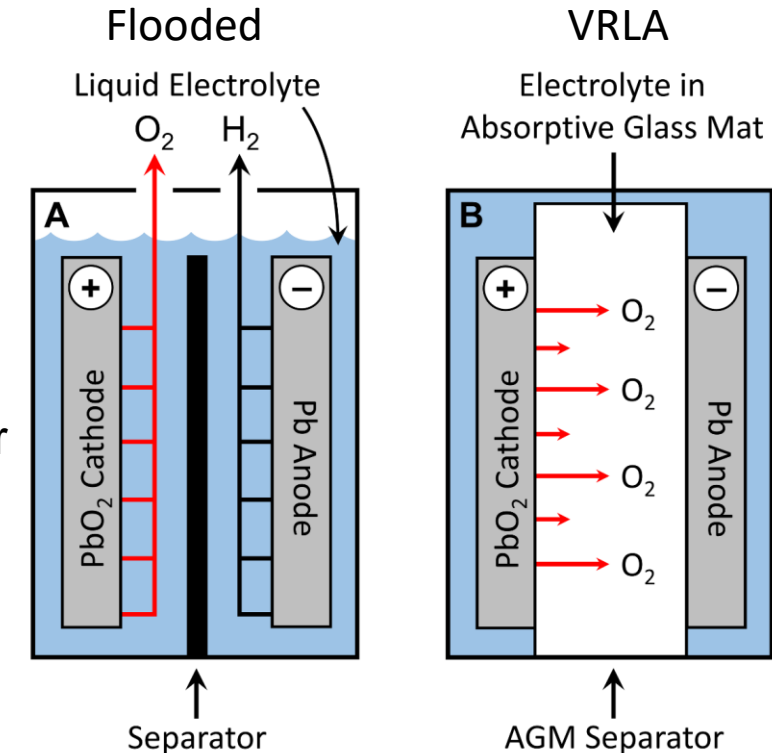
# Aqueous lead-acid batteries

- Lead-acid batteries had the largest rechargeable battery market share in both sales and capacity in 2017
- Lead-acid batteries have a low material cost, low self-discharge rate, and function over a wide range
- Due to toxicity, 99% of all Lead-acid batteries are recycled making up 60% of all lead production
- Mechanistically,  $PbO_2$  is reduced to  $Pb^{2+}$  which chemically reacts with the sulfuric acid electrolyte at the cathode and  $Pb$  is oxidized to  $Pb^{2+}$  at the anode
- Challenges:
  - Intrinsic low energy density (30 Wh/kg) due to weight of lead
  - Operation at partial states of charge (PSoC) shortens battery life due to irreversible growth of large  $PbSO_4$  crystals
  - Charge and discharge rates are low compared to other technologies



# Aqueous lead-acid batteries

- Two types of lead-acid batteries are used, flooded and valve-regulated (VRLA)
- Flooded cells have electrodes suspended in a large amount of electrolyte in an open case structure allowing for gas to vent
- VRLA cells are sealed and use a pressure release valve to prevent excessive gas buildup
- Through careful control of charging voltage and current collector material, water reduction/oxidation can be minimized to prevent loss of electrolyte to gas evolution
- A recent advancement in the technology is the incorporation of conductive carbon in with the Pb anode



J. O. G. Posada, A. J. R. Rennie, S. P. Villar, V. L. Martins, J. Marinaccio, A. Barnes, C. F. Glover, D. A. Worsley, P. J. Hall, *Renewable and Sustainable Energy Reviews*, vol. 68, pp. 1174-1182, 2017.

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V. F. K. Mongird, V. Viswanathan, V. Koritarov, P. Balducci, B. Hadjerioua, J. Alam "Energy Storage Technology and Cost Characterization Report," 2019.

# Aqueous Ni-based batteries

- There are three main types of aqueous Ni batteries: nickel-iron (NiFe), nickel-cadmium (NiCd), and nickel metal hydride (NiMH)
- All three have higher specific energies than lead-acid, but all have lower voltages (lead-acid: 30 Wh/kg, 2.05V)
- NiFe has the lowest specific energy, but material cost is very low and maintains a low environmental impact and long cycle life, this has resulted in its adoption for smaller-scale stationary energy storage
- Some grid-scale NiCd systems were installed, however most have been decommissioned due to the well known memory effect which forces NiCd batteries to be ineffective for PSoC operation
- Although NiMH yields the highest specific energy, the elevated cost of production has kept its grid-scale use to a minimum

	Specific energy (Wh/kg)	Voltage (V)
NiFe	30-50	1.05
NiCd	50	1.2
NiMH	100	1.2

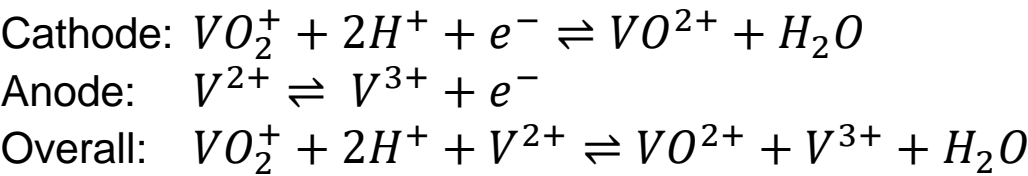
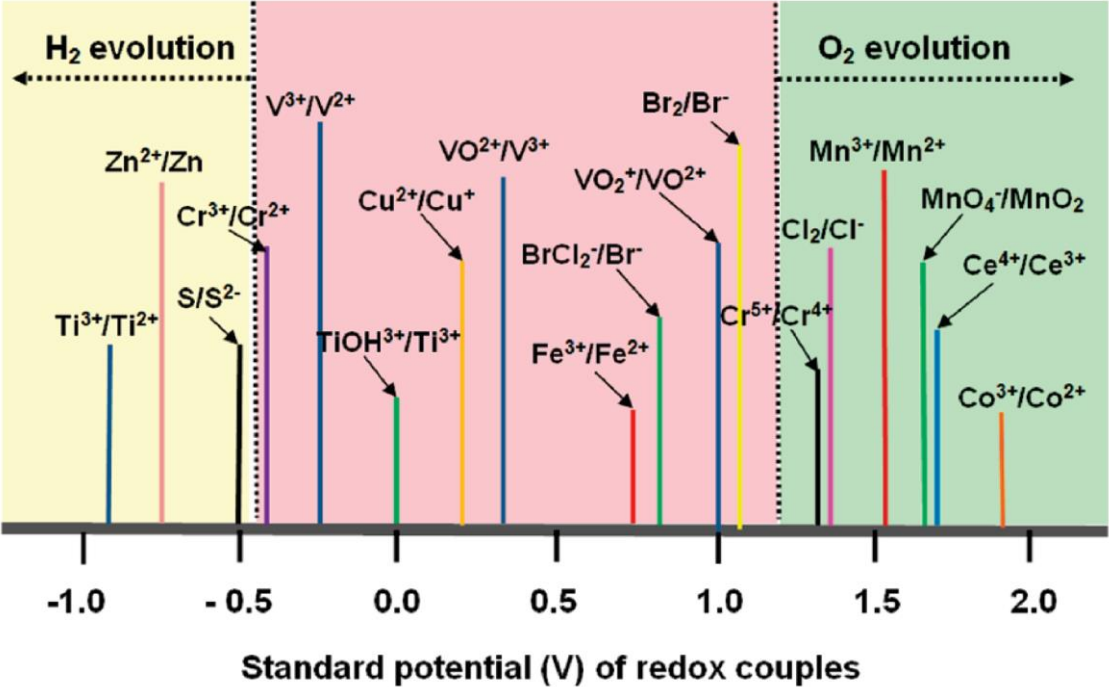
J. O. G. Posada, A. J. R. Rennie, S. P. Villar, V. L. Martins, J. Marinaccio, A. Barnes, C. F. Glover, D. A. Worsley, P. J. Hall, *Renewable and Sustainable Energy Reviews*, vol. 68, pp. 1174-1182, 2017.  
F. Beck, P. Rüetschi, *Electrochimica Acta*, vol. 45, no. 15, pp. 2467-2482, 2000.  
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# Redox flow batteries (RFB)

- Unlike traditional batteries, the redox active species in RFBs are liquids flowing over current collectors
- All-vanadium redox battery (VRB) have seen the most development, with >1mW systems in operation
- The VRB has seen the most use because of its high cycle life, round-trip efficiency, and low self discharge
- Other RFBs that have seen >100kW deployment include: zinc/bromine (ZBB), polysulfide/bromine (PSB), and iron/chromium (ICB)

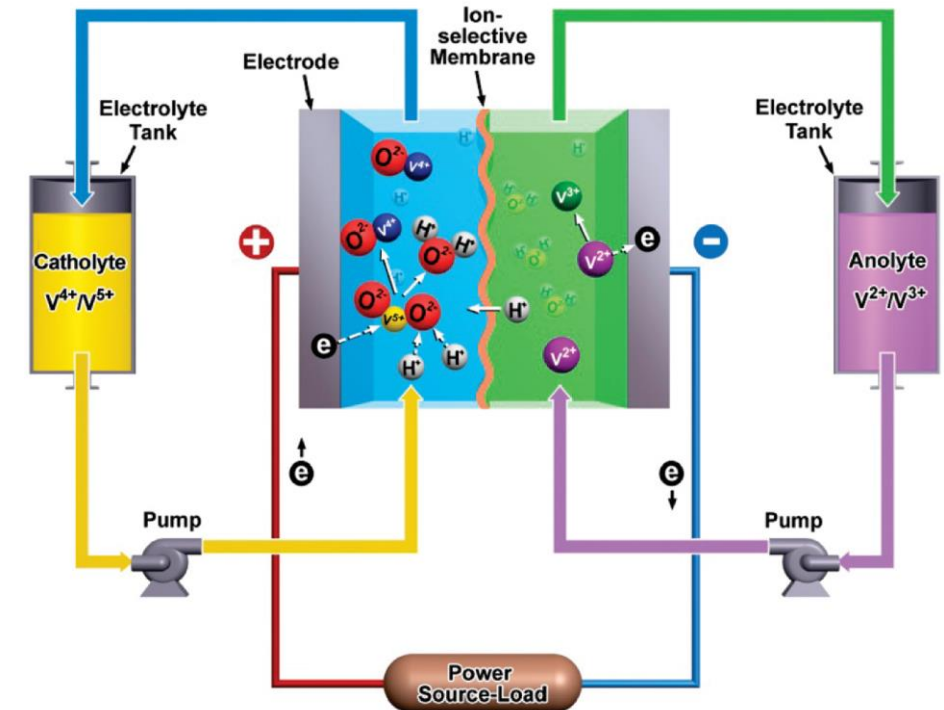
Type	OCV (V)	Specific energy (Wh/kg)	Discharge time (h)	Self-discharge% per month at 20° C	Cycle life	Round-trip DC energy efficiency
VRB	1.4	15 (29)	4-12	5-10	5000	70-80%
PSB	1.5	20 (41)	4-12	5-10	2000	60-70%
ICB	1.18	<10	4-12		2000	70-80%
ZBB	1.8	65 (429)	2-5	12-15	2000	65-75%



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X.-Z. Yuan, C. Song, A. Platt, N. Zhao, H. Wang, H. Li, K. Fatih, D. Jang, *Int J Energy Res* vol. 43, no. 13, pp. 6599-6638, 2019.

# Redox flow batteries (RFB)

- RFB systems are attractive because capacity can be increased by increasing catholyte and anolyte volume, and rate can be varied by current collector area leading to a highly flexible system
- In RFBs, catholyte and anolyte are pumped from storage tanks over electrodes and are separated by ion-selective membranes
- The electrodes require high conductivity and surface area and are therefore typically porous or felt carbon
- The membrane has many important requirements including: high ionic conductivity, ion selectivity, limited water transport, and chemical and mechanical stability
- For VRB, the typical membrane is Nafion and Nafion hybrids due to the highly acidic electrolytes
- Membrane adds significant cost to the battery system



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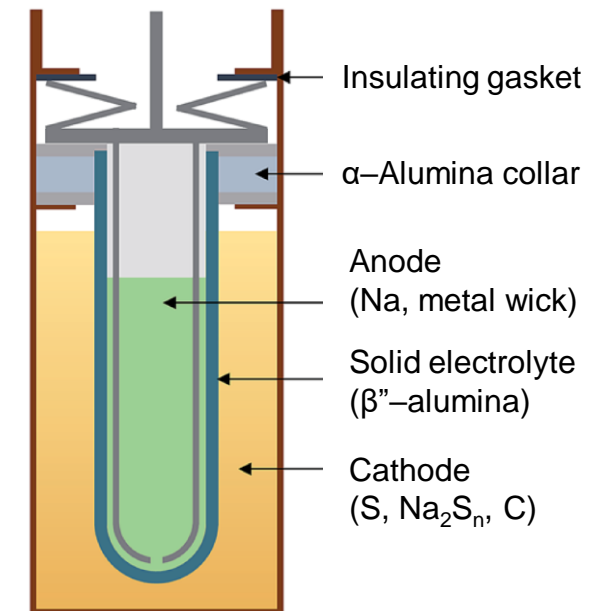
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V. F. K. Mongird, V. Viswanathan, V. Koritarov, P. Balducci, B. Hadjerioua, J. Alam "Energy Storage Technology and Cost Characterization Report," 2019.

# High temperature sodium batteries (NaS)

- High temperature NaS batteries utilize molten Na and S at  $\sim 300^\circ\text{C}$ , below  $280^\circ\text{C}$ , the polysulfide melt will solidify
 

$2\text{Na} + 5\text{S} \rightleftharpoons \text{Na}_2\text{S}_5$	$E=2.076\text{V}$ at $300^\circ\text{C}$
$2\text{Na} + 4\text{Na}_2\text{S}_5 \rightleftharpoons 5\text{Na}_2\text{S}_4$	$E=1.970\text{V}$ at $300^\circ\text{C}$
$2\text{Na} + 3\text{Na}_2\text{S}_4 \rightleftharpoons 4\text{Na}_2\text{S}_3$	$E=1.74\text{-}1.81\text{V}$ at $300^\circ\text{C}$
- The NaS system has a theoretical capacity of 760 Wh/kg, which is significantly higher than lead-acid or Ni-based systems
- During operation  $\text{Na}^+$  migrates through the solid electrolyte to form various polysulfides, these systems intentionally do not go to lower polysulfides than  $\text{Na}_2\text{S}_3$  due to irreversible precipitation of lower polysulfides
- Naturally, due to the high temperature a large portion of the capital cost of NaS batteries goes toward insulation and safety precautions
- Additionally,  $\sim 15\%$  of the capacity is used each day to keep the battery at the requisite temperature



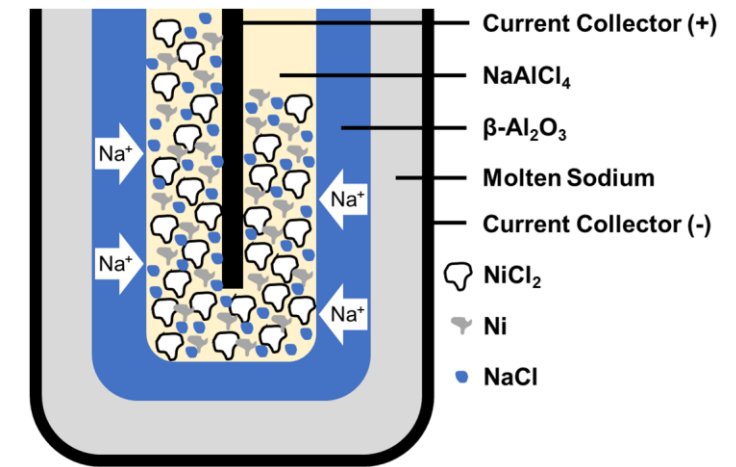
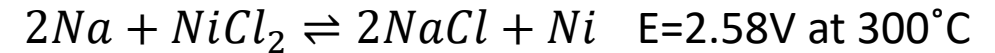
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# High temperature sodium batteries (ZEBRA)

- Zero-emission battery research activities (ZEBRA) are Na-NiCl<sub>2</sub> cells and also require high temperatures and molten Na
- The 2 e<sup>-</sup> process in the ZEBRA results in a lower capacity than NaS, however due to the increased voltage of 2.58 vs. 2.1, the theoretical energy density is slightly higher at 788 Wh/kg
- The cell design is inverted from the NaS cell, with molten Na on the exterior and Ni species on the interior still separated by the same β-alumina solid electrolyte
- Similar to the NaS system, there are high costs associated with insulation and safety procedures due to the elevated temperature required
- The limiting temperature in ZEBRAs is 157°C for NaAlCl<sub>4</sub>, as such literature reports showed feasibility of a reduced operating temperature of 190°C which would lead to decreased costs



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# Na-ion batteries

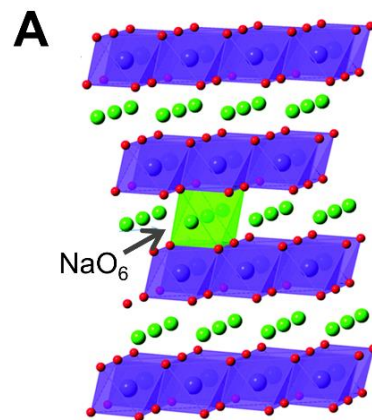
- Na is vastly more abundant and well distributed on earth than Li causing Na to be a fraction of the cost of Li (>85% cost reduction)
- Na-ion batteries utilize the similar properties of Na and Li, and the vast knowledge base already acquired on Li-ion batteries
- The commonly studied Na-ion electrolytes are sodiated versions of Li-ion electrolytes (ex.  $\text{NaPF}_6$  in EC:DMC vs.  $\text{LiPF}_6$  in EC:DMC)
- Electrode materials do not translate from Li-ion to Na-ion as well because  $\text{Na}^+$  has a larger ionic radius which causes difficulties with reversible intercalation
- For the anode,  $\text{Na}^+$  cannot reversibly intercalate into graphite, however disordered hard carbons is an effective substitute to graphite and maintains a capacity of >200 mAh/g

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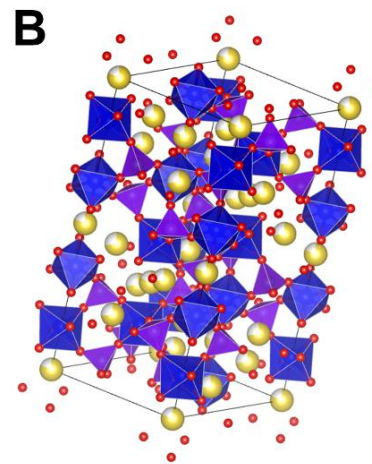
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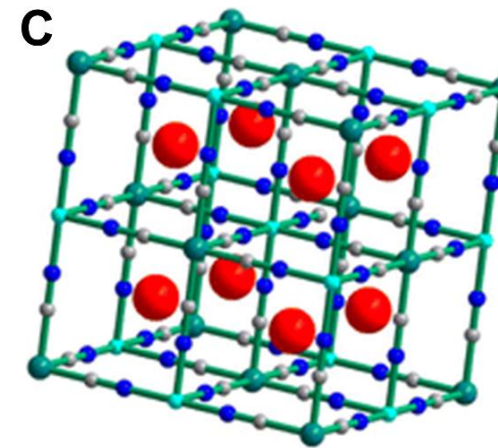
# Na-ion batteries



Layered transition metal  
oxide (ex:  $\text{NaMnO}_2$ )



Polyanionic structure  
(ex:  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ )



Prussian Blue analog  
(ex:  $\text{Na}_2\text{Co}[\text{Fe}(\text{CN})_6]$ )

- The key to Na-ion commercialization is identification and optimization of a suitable cathode material
- Currently no Na-ion cathode is capable of supporting high capacities, rate capabilities, long cycle lives, and cost-effective synthetic strategies

J. Chen, D. H. C. Chua, P. S. Lee, *Small Methods*, vol. 4, no. 1, 2020.

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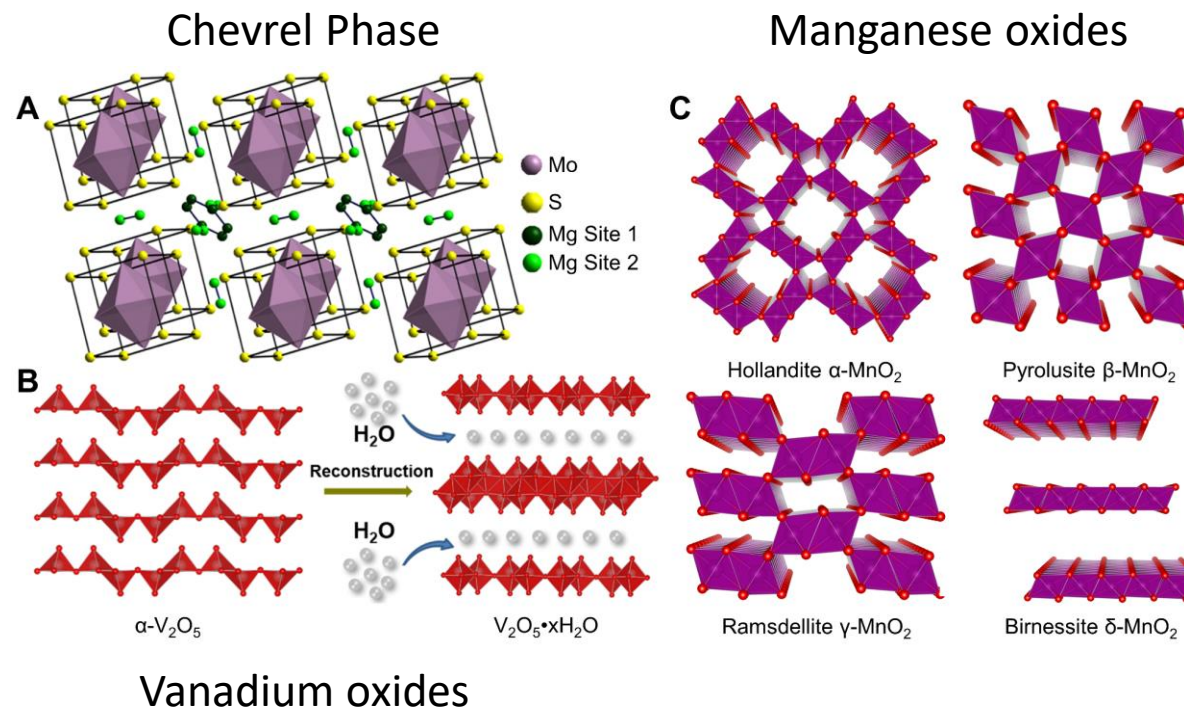


## Rechargeable magnesium batteries (RMB)

- RMBs are highly attractive due to their divalent ion carrier, Mg's high elemental abundance (5<sup>th</sup> in the earth's crust), and metal anode
- Unlike alkali metals, dendrite free plating and stripping is achievable for a Mg metal anode, Mg is more stable to ambient atmosphere and forms less toxic compounds, and a Mg metal anode allows for high theoretical capacities (2200 mAh/g, 3835 mAh/cm<sup>2</sup>)
- The reduction potential for Mg is still high at -2.4 V (Li, -3.05 V)
- Typical Li-ion electrolyte analogs are incompatible for RMBs (ex. Mg(PF<sub>6</sub>)<sub>2</sub> in EC:DMC), causing thick insulating passivation layers
- Extensive research has found that organo-magnesium complexes in THF work well however many have low voltage stability windows <2.5 V vs. Mg/Mg<sup>2+</sup> which limits operating voltage
- Some of the common promising electrolytes are Bu<sub>2</sub>Mg:EtAlCl<sub>2</sub>, PhMgCl:AlCl<sub>3</sub>, or MgCl<sub>2</sub>:AlCl<sub>3</sub>
- Although these electrolytes can effectively shuttle Mg<sup>2+</sup> with minimal electrolyte degradation on the anode, they are extremely corrosive forcing the use of carbon-based current collectors

# Rechargeable magnesium batteries (RMB)

- The small ionic radius of  $\text{Mg}^{2+}$  paired with the 2+ charge leads to strong electrostatic interactions causing both desolvation and deinsertion challenges
- For this reason, the commonly studied cathode materials for RMBs are different than typical Li-ion cathodes
  - Chevrel phase (ex.  $\text{Mg}_2\text{Mo}_6\text{S}_8$ ) offer long cycle lives with high-capacity retention, however, have low voltages (1.1V) and capacities (<100 mAh/g)
  - Vanadium oxides (ex.  $\text{V}_2\text{O}_5$ ) have higher voltages (2-3V) and capacities (150-300 mAh/g), but typically have poor cycle lives
  - The many structures of manganese oxides (ex.  $\text{MnO}_2$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MgMn}_2\text{O}_4$ ) offer a wide range of capacities and voltages, however all suffer from short cycle lives (<50 cycles)
- The key to commercialization of RMBs is the correct pairing of cathode material and electrolyte that offers a large enough voltage range and long cycle life



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## Rechargeable aqueous zinc batteries (RAZB)

- Similar to the rechargeable magnesium battery, RAZBs utilize a zinc metal anode and the divalent  $\text{Zn}^{2+}$  charge carrier
- The RAZB also uses an aqueous electrolyte which severely decreases cost while improving safety
- The reduction potential of Zn is -0.76 which is negative of the water reduction potential, and although  $\text{H}_2$  evolution is a side reaction, the poorly catalytic Zn surface for water reduction aids in suppression of  $\text{H}_2$  evolution
- The Zn metal anode is less ideal than the Mg metal anode and does form dendritic growth, the dendrites can penetrate the separator shorting the battery or break away orphaning Zn metal
- The literature typically employs 3D anode structures to mechanically suppress dendrites or surface layers to inhibit the rapid growth
- There are two main electrolyte conditions used for RAZB alkaline (pH 14) and mildly acidic (pH 4)
  - Alkaline RAZBs mimic the standard primary Zn/ $\text{MnO}_2$  cells
  - Mildly acidic RAZBs have a wider range of cathodes to work with but all use either 2M  $\text{ZnSO}_4$  or 3M Zn triflate

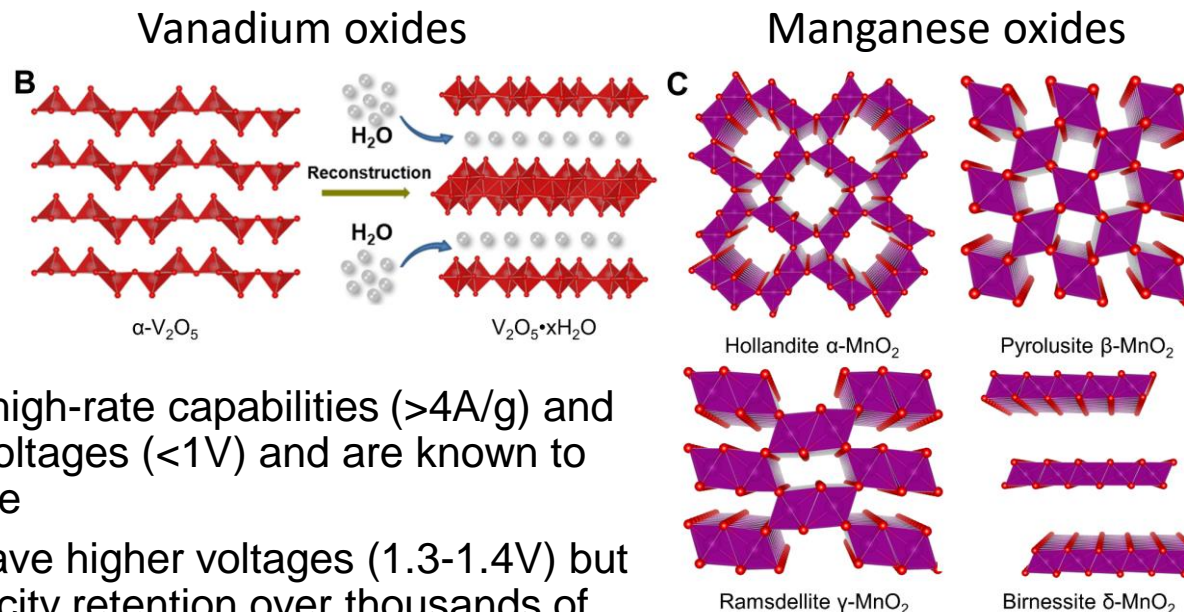
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# Rechargeable aqueous zinc batteries (RAZB)

- Similar to  $\text{Mg}^{2+}$ , the  $\text{Zn}^{2+}$  ion's increased electrostatic interactions causes challenges for deintercalation
- For this reason, vanadium and manganese oxides with large layers and tunnel structures are effective cathodes
  - Vanadium oxides (ex.  $\text{V}_2\text{O}_5$ ,  $\text{V}_3\text{O}_8$ ) offer very high-rate capabilities ( $>4\text{A/g}$ ) and high capacities ( $>300\text{ mAh/g}$ ), but have low voltages ( $<1\text{V}$ ) and are known to dissolve over time and passivate the Zn anode
  - Manganese oxides (ex.  $\text{MnO}_2$ ,  $\text{K}_{0.8}\text{Mn}_8\text{O}_{16}$ ) have higher voltages ( $1.3\text{-}1.4\text{V}$ ) but lower capacities ( $200\text{-}300\text{ mAh/g}$ ). High-capacity retention over thousands of cycles has been observed at reasonable rates ( $1\text{-}2\text{A/g}$ )
  - $\text{MnO}_2$  is also known to dissolve over time, however the addition of  $0.1\text{ M MnSO}_4$  is effective at suppressing Mn dissolution which allows for the long cycle lives
- Grid-scale development and instillation is already underway using Zn/ $\text{MnO}_2$  batteries in an alkaline electrolyte with a 1 MWh system in construction for the City University of New York



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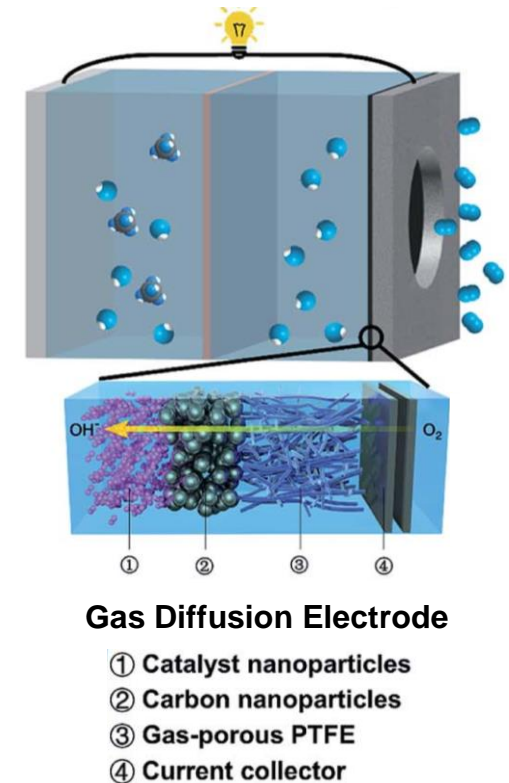
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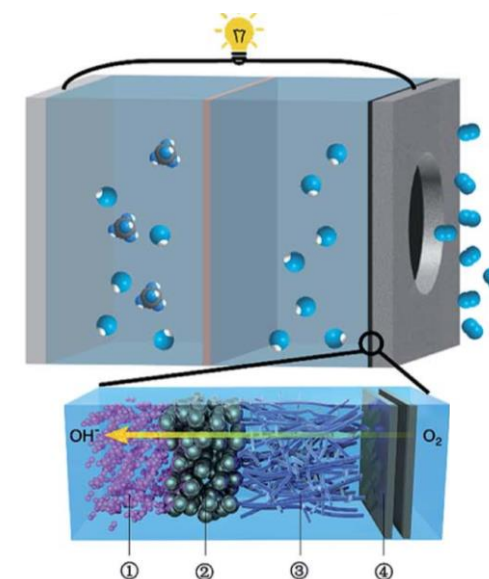
# Metal-air batteries

- Metal-air batteries are attractive due to the high theoretical energy densities (ex. Zn-air, 1353 Wh/kg), and potentially low fabrication costs
- Metal-air batteries consist of a metal anode, a porous gas diffusion cathode, and an aqueous or nonaqueous electrolyte
- The main metal-air batteries being tested are Li, Na, K, Mg, Al, Fe, and Zn
- Typically, Fe and Zn use an aqueous electrolyte while Li, Na, K, Mg, and Al use a nonaqueous electrolyte because of their more negative reduction potentials
- The Zn-air battery utilizing an alkaline aqueous electrolyte is currently the only technology being deployed, but only at the small scale (NantEnergy)
- Although the NantEnergy cells have a theoretical capacity of 1353 Wh/kg, their reported energy density is only ~35 Wh/kg



# Metal-air batteries

- For the Zn-air battery
  - The Zn metal anode has similar challenges to the RAZB with dendritic growth and passivation layers formed due to water reduction
  - The air cathodes are constructed by loading electrocatalysts onto porous PTFE
    - Porous PTFE allows for fast permeation of  $O_2$  throughout the cathode
    - The catalyst must be efficient at both ORR and OER
    - Some examples of catalyst are, Pt,  $MnO_2$ ,  $LaMnO_3$ , metal free carbonaceous materials, and transition metal oxides and sulfides
    - Under real working conditions, only a low round-trip efficiency of <65% is achieved
  - The aqueous electrolyte used in Zn-air batteries is concentrated alkaline solution which aids the efficiency of the ORR and OER reactions
- Due to cathode poisoning by  $CO_2$  and irreversible solid formation, most metal-air batteries have short lifetimes
- Fe-air is another interesting metal air system, with a low practical energy density of 60-80 Wh/kg, but it is the lowest cost metal-air system (<\$100/kWh), highest cycle life system (>1000 cycles), and is environmentally benign



**Gas Diffusion Electrode**

- ① Catalyst nanoparticles
- ② Carbon nanoparticles
- ③ Gas-porous PTFE
- ④ Current collector

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# Conclusions

- To fully integrate renewable energy sources into the grid, an increase in energy storage systems need to be implemented
- Cost-effective GSEESS technology is still needed, since the stationary application of Li-ion batteries and redox flow technologies are costly
- Improvements in materials sourcing and cell design are required for many of the presented technologies to reduce cost for grid-scale development
- Both system stability and safety are critical factors which demand further investigation, particularly for the redox flow cell and Li/Na-ion technologies
- **To achieve a system with high safety, low cost, and long cycle life; both fundamental and applied research is required both on high and low technology readiness level GSEESSs**



# Acknowledgements



**Dr. Imre Gyuk**  
Energy Storage Program Manager  
Office of Electricity Delivery and Energy Reliability  
U.S. Department of Energy



**Dr. Babu Chalamala**  
Manager, Energy Storage Technology  
and Systems Department  
Sandia National Laboratories

**Dr. Eric Sporerke**  
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